

The Constitution of Sulphur Vapour.

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[PLATES 13 AND 14.]

The constitution of sulphur vapour has been studied by many investigators, the method usually employed being based upon the determination of the density.

In 1835 Dumas and Mitscherlich found the vapour density at temperatures near the boiling point to be 6.56, which corresponds closely with the molecular formula S_8 . Deville and Troost carried out determinations at temperatures ranging from 860°C . to 1040°C . and obtained the value 2.23 which is that required by the formula S_2 . More recently Biltz* has shown that below 800°C . the density is greater than is required by the formula S_2 , and at 468°C . becomes 7.8 which corresponds approximately to the formula S_7 , without any constant value being observed between these temperatures. Bleier and Kohn† found that when determinations were made under reduced pressure between 192°C . and 310°C . the density of the vapour gradually rose with increase of pressure and slowly but asymptotically approached the value S_8 . Evidence of the existence of molecules containing eight atoms has also been obtained from an examination of solutions of sulphur. Biltz holds that the value obtained by Dumas and Mitscherlich is only of significance for the conditions of temperature and pressure under which it was determined, and affords no evidence of the presence of hexatomic molecules in the vapour. His view is that only octatomic and diatomic molecules have any existence, the former gradually dissociating into the latter as the temperature is raised until about 900°C ., the dissociation of the heavier molecules is complete and the vapour is composed entirely of diatomic molecules. Above this temperature no further change appears to occur. Preuner, on the other hand, from a study of the curve representing the change of density with change of pressure‡ considers that it is not unlikely that hexatomic and tetraatomic molecules are formed as intermediate products of the dissociation of the octatomic molecules. Of this, however, the investigation of the vapour density does not afford any conclusive evidence.

* 'Zeit. Phys. Chem.,' vol. 2, p. 920 (1888).

† 'Monatsh. Chem.,' vol. 21, p. 575 (1900).

‡ 'Zeit. Phys. Chem.,' vol. 44, p. 733 (1903).

The colour of sulphur vapour passes through a remarkable series of changes as the temperature is raised. According to Howe and Hammer* it is orange yellow just above the boiling point, deep red at 500° C., and straw yellow at 634° C. The method followed in their experiments, however, did not admit of any great degree of accuracy in the measurement of the temperature at which the changes of colour occur, and no attempt apparently has hitherto been made to correlate these changes with the changes of molecular complexity which occur as the temperature of sulphur vapour is raised. In a paper contributed to the Society in 1910 by Mr. J. I. Graham, B.Sc.,† the author described the narrow absorption bands with which the spectra of sulphur vapour abound, and from an examination of their distribution under various conditions of temperature and pressure concluded that they form two systems, one belonging to molecules of the formula S_8 , the other to molecules of the formula S_2 . At atmospheric pressure he found no evidence of the presence of any other molecules. At reduced pressures, on the other hand, the spectra obtained below 520° C., gave evidence, he considered, of the existence of molecules intermediate in complexity between the octatomic and the diatomic molecules. The paper makes no reference to the phenomena of the colour changes which appear to us to afford the only satisfactory evidence of the existence of such molecules, and it is with these phenomena that the present paper principally deals.

In the method of experimenting adopted, the sulphur under examination was placed in a silica tube 100 mm. long and 12 mm. in diameter, closed at each end by a flat ground silica plate fused on to the tube. A weighed quantity of sulphur having been introduced through a narrow side tube, the air was displaced by nitrogen, the tube evacuated to 8 mm. and sealed. It was then placed in the silica or porcelain tube of a small electric resistance furnace, the space between the inner and outer tubes being packed with asbestos to prevent any light reaching the spectroscope except through the inner tube. This tube was arranged so that its axis was in line with that of the collimator of the spectrograph used for photographing the spectra, and the light to be examined after passing through the tube was directed by means of a lens upon the slit of the collimator. The arrangement will be readily understood from the accompanying diagram (fig. 1).

Various sources of light were employed, that of the Nernst filament being found most generally convenient for the visible spectrum and the ultra-violet as far as λ 3100. For observations beyond the range of the Nernst filament, a cadmium arc proved most suitable, not only because the spectrum

* 'J. Amer. Chem. Soc.,' vol. 20, p. 757 (1898).

† 'Roy. Soc. Proc.,' A, vol. 84, p. 311 (1910).

of cadmium reaches far down into the ultra-violet, but because it possesses a continuous background upon which the most delicate bands can be readily observed. It is possible that the strong lines of the cadmium spectrum may conceal bands which happen to coincide nearly with them in position, but we know of no other convenient source of light which is free from this objection and extends far enough into the ultra-violet for our purpose.

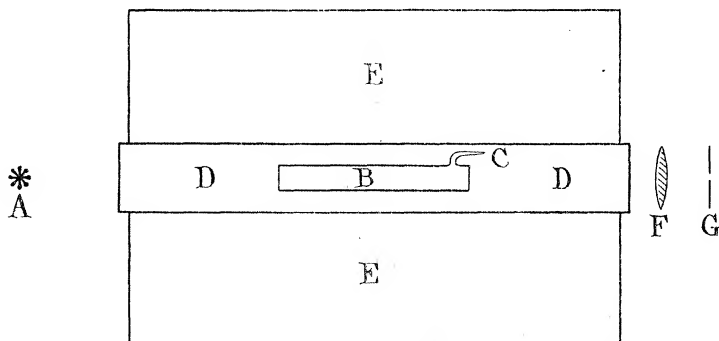


FIG. 1.—A, source of light; B, silica tube containing sulphur; C, side tube for introducing sulphur; D, tube of electrical resistance furnace packed with asbestos; E, case of furnace filled with magnesia bricks; F, quartz lens to slit of spectrograph.

The instrument employed in the experiments was a large Hilger quartz spectrograph. The temperature of the sulphur vapour was ascertained by means of a platinum—platinum rhodium thermo-couple placed in intimate contact with the tube containing the sulphur.

Photographs of the spectrum of the light from the Nernst filament or cadmium arc were taken, after its passage through the sulphur vapour, at approximately equal intervals of temperature between 400° C. and 1200° C. The weights of sulphur employed in the experiments were 0.5, 1.0, 2.0, 4.0, and 8.0 mgrm. Fig. 2 shows the results obtained with 1 mgrm. of sulphur. The successive bands of the figure represent the spectra at the temperatures marked opposite to them. From an inspection of these it will be seen that the effect of raising the temperature is very remarkable. At first there is an increase in the absorption, in other words, the spectrum transmitted becomes shorter as the temperature rises. At the same time the colour gradually changes from orange yellow to red. The shortening of the spectrum continues and the depth of the colour increases until a certain temperature is reached when the effect is reversed, the vapour then becomes more and more transparent, the length of the spectrum increases, and the colour changes again to light yellow as the temperature is raised. The temperature at which the reversal of the phenomena occurs

has been found, as the result of many experiments, to be somewhere near 650°C . The effect of increasing the quantity of sulphur in the tube to 8.0 mgrm. is, as will be seen from inspection of fig. 3, to increase the general absorption and, as it were, push back the curve towards the red end of the spectrum. At the same time the shortening of the spectrum in the red becomes pronounced. But the general result is the same; the absorption first increases to a maximum at or near 650°C . and then falls off. Numerous experiments made with other quantities of sulphur gave results similar to those shown in figs. 2 and 3 (Plate 13).

In each of the series of experiments to which figs. 2 and 3 refer the weight and volume of the sulphur vapour was the same throughout. It is to be observed that while each spectrum in figs. 2 and 3 is the spectrum of the light after its passage through a layer of the same depth containing the same weight of sulphur, the pressure was different in each case, and this may have influenced to some extent the course of events. The influence cannot, however, have been great within the limits of pressure obtaining in our experiments, and we found in every case, whether operating with 0.5 mgrm. or 8 mgrm. of sulphur, that the point of maximum absorption lay near 650°C . Whatever alteration of the maximum point the alteration of pressure produces is therefore clearly too small to be measurable by the method employed by us.

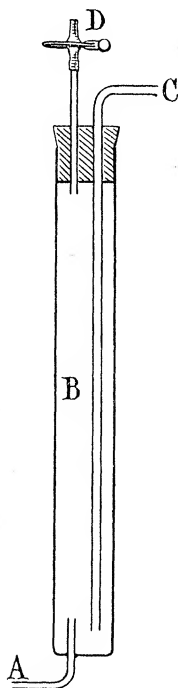


FIG. 4.—A, silica tube for connecting with C in fig. 1; B, silica tube filled with nitrogen; C, inlet for nitrogen; D, rubber tube closed by pinch-cock.

One series of experiments was carried out at the atmospheric pressure. For this purpose, the usual apparatus was modified, as shown in fig. 4. The tube containing the sulphur vapour was connected by means of a silica tube of narrow diameter with a reservoir of nitrogen, which was so arranged that equilibrium could readily be established by means of a stopcock between the pressure of the gases inside the tube and that of the atmosphere. As the temperature of the furnace was raised, some of the

sulphur vapour distilled into the side tube connecting with the nitrogen reservoir, where it was allowed to condense, but kept liquid by means of a small gas jet. The plug of liquid sulphur thus formed prevented any nitrogen getting into the observation tube while allowing of the expansion of the

sulphur vapour. In this experiment the effect of varying pressure was eliminated, but the fact that the quantity of sulphur in the observation tube altered with the temperature introduced another source of complication. While the different spectra in this case are not those of equal quantities of sulphur, the variation in the amount of sulphur is not great enough to overpower the effect of temperature at 650°C ., at which the maximum absorption is again seen to occur (fig. 5).

The remarkable series of changes which the spectra undergo with rise of temperature can only be explained by assuming changes in the molecular constitution of the vapour. If, however, Biltz's view that only two kinds of molecule S_8 and S_2 exist be correct, we should expect the spectrum to lengthen or shorten continuously as the one form passes into the other under the influence of change of temperature. The fact that it first becomes shorter with rise in temperature, in other words, that the absorption increases up to a certain point and that then it lengthens, the absorption diminishing when that point is passed, can hardly admit of any other explanation than that molecules of some degree of complexity intermediate between those of S_8 and S_2 and more highly absorptive than either, are formed as intermediate products of dissociation.

The fact that Biltz did not find any constant value for the density of the vapour between 468°C . and 800°C . does not preclude the possibility of the existence of molecules other than S_8 and S_2 , stable only over a comparatively limited range of temperature. He made no determinations apparently between 606°C . and 1400°C ., but it is a remarkable circumstance that the density value for the temperature 650°C . found by extrapolation of his curve is 3.4, which is very nearly that required by the formula S_3 . By itself this is perhaps of little import, but it acquires significance when taken in conjunction with the fact that precisely at the temperature at which the vapour possesses this density it also possesses optical properties distinct from those of the vapour composed of molecules of diatomic or octatomic sulphur. The evidence for the existence of triatomic sulphur, which is thus indicated, is strengthened if we take account of the analogies between sulphur and oxygen. As is well known, ozone possesses much greater absorptive power for light than ordinary diatomic oxygen.* Now, if we assume the existence of triatomic molecules of sulphur constituted in the same way as ozone, we should expect them to possess greater absorptive power than those of diatomic sulphur, and this condition, as we have seen, is fulfilled by sulphur vapour at 650°C .

As has already been mentioned, the spectra of sulphur vapour exhibit

* Hartley, 'J. Chem. Soc.', vol. 39, pp. 57, 111 (1881).

numerous bands, both in the visible and in the ultra-violet regions. The following is a list of the bands given by the spectra of 2 mgrm. of sulphur at a few of the temperatures between 485° C. and 1150° C. at which observations were made :—

1030° C.	830° C.	650° C.	485° C.
4849 <i>f</i>	4970	4989 <i>f</i>	4755
4784 <i>f</i>	4910	4960 <i>f</i>	4685 <i>w</i>
4714 <i>f</i>	4840	4885	4555
4679 <i>f</i>	4763	4820 <i>w</i>	4520
4655 <i>f</i>	4705	4750 <i>w</i>	4496
4640 <i>f</i>	4665	4714	4480
4620 <i>f</i>	4640	4685	4455
4595 <i>f</i>	4630 <i>w</i>	4650	4445 <i>w</i>
4586 <i>f</i>	4603	4635	4410
4549 <i>f</i>	4580	4611	4379
4530 <i>f</i>	4555	4595	4360
4505	4540	4560 <i>w</i>	4340
4485	4520	4535	4311 <i>w</i>
4458	4500	4520	4307
4435	4480	4500	4276
4420	4450 <i>w</i>	4480	4255
4410	4420	General absorption after λ 4430	4240
4394	4410		General absorption after λ 4220
4370	4379	One very wide band with centre about λ 5190	
4360	4365		
4340	4355		
4320	4340		
4311	General absorption after λ 4220		
4276			
4261			
4242			
4230			
4215			
4189			
4150			
4127			
4085			
4045			
4039			
4020			
3960			
3890			
3790 <i>f</i>			
3720 <i>f</i>			
3681 <i>f</i>			
General absorption after λ 3630			

f = faint band.

w = wide band.

From an examination of this list it will be observed that some of the bands occur in all the spectra. Seeing that no further change takes place in the spectra above 900° C., and that the density of sulphur vapour at that temperature corresponds with the molecule S₂, it may be assumed that the bands which occur at 900° C. are the bands of S₂, and inasmuch as these same

bands also occur at the lowest temperatures at which the vapour was examined, we have here direct evidence that the dissociation into molecules S_2 begins at or immediately above the temperature at which the sulphur vapourises.

With very small quantities of sulphur (0.5 mgrm.) interesting phenomena are observed in the ultra-violet region, which of course cannot be studied when larger quantities are employed. At temperatures below 650°C . no absorptive effect whatever can be detected in any part of the cadmium spectrum; at 650°C . there is a slight weakening of the spectrum at $\lambda 2824$; and 100° higher a series of clearly defined narrow absorption bands make their appearance at $\lambda 3027$, $\lambda 2834$, $\lambda 2886$, $\lambda 2762$, $\lambda 2730$, $\lambda 2702$, and $\lambda 2628$. These bands become beautifully distinct at 855°C . They can still be traced at 1010°C ., but not so clearly, owing to the whole spectrum beyond $\lambda 2750$ being only faintly transmitted. At higher temperatures there is general absorption beyond $\lambda 2940$, and only the bands nearest the red end can be seen. Using the Nernst filament as the source of light, similar phenomena are observed with a somewhat different arrangement of the bands. At 650°C . there is one band at $\lambda 3422$. At 700°C . bands occur at $\lambda 3422$, $\lambda 3398$, $\lambda 3369$, $\lambda 3348$, $\lambda 3314$, and $\lambda 3298$. The number of bands increases as the temperature is raised, the maximum occurring at 900°C .

Bands observed with 0.5 mgrm. sulphur, using a Nernst filament.

1015° C.	900° C.	800° C.	700° C.	650° C.
3875	3775	3422	3422	3422 only and very faint
3775	3675	3398	3398	
3675	3605	3380	3369	
3605	3570	3369	3348	
3570	3510	3348	3314	
3510	3480	3329	3298	
3480	3456	3314		
3456	3440	3298		
3440	3422	3290		
3422	3398	3272		
3398	3380	3256		
3380	3369	3230		
3369	3348	3217		
3348	3329	3183		
3329	3314	3156		
3314	3298	3136		
3298	3290			
3290	3272			
3272	3256			
3256	3230			
General absorption after $\lambda 3050$	3217			
	3197			
	3183			

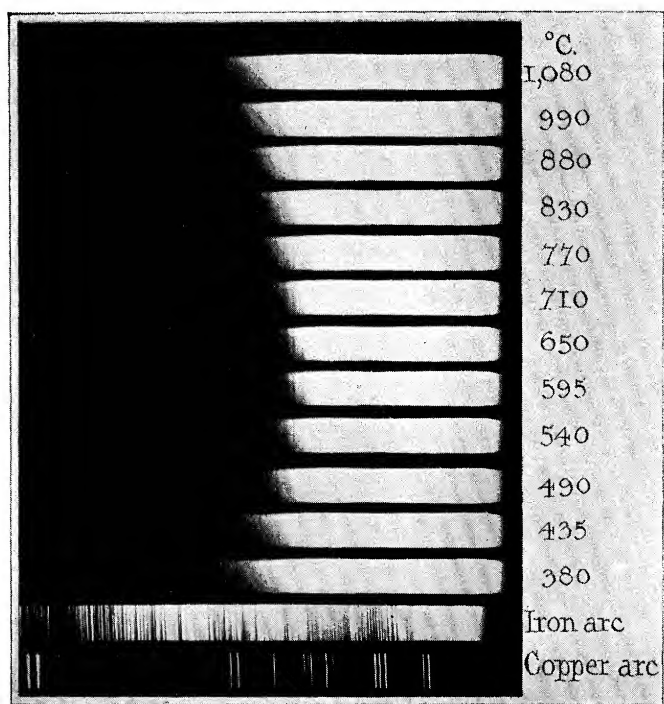


FIG. 2.

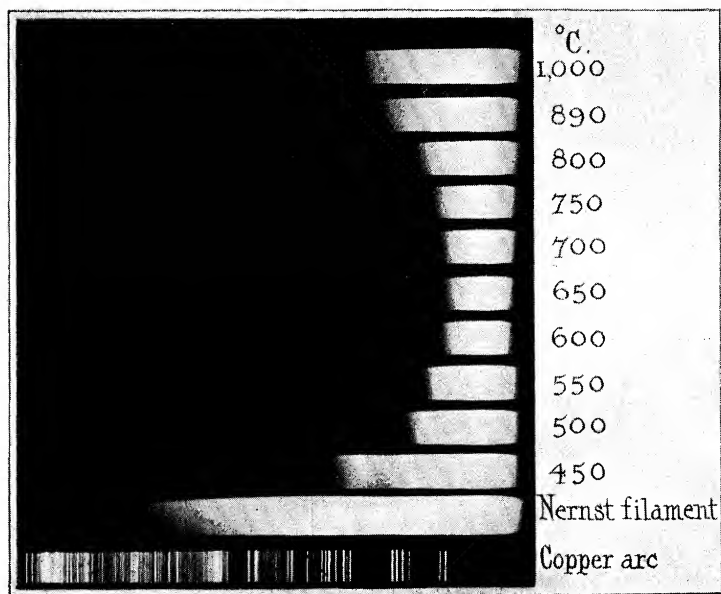


FIG. 3.

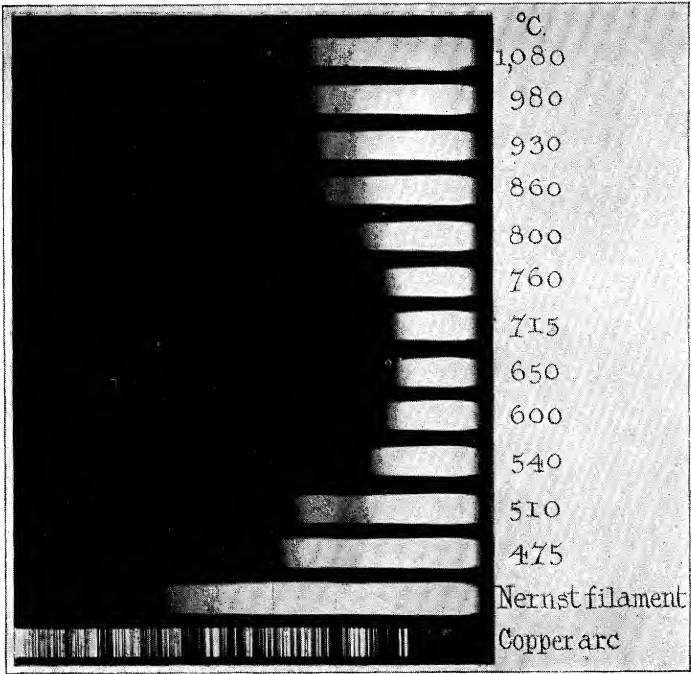


FIG. 5.

Above 900° C., as already stated, no further change is to be observed in the spectra, and we conclude that at that temperature all the molecules are in the diatomic state as indicated by the vapour density determinations. The spectroscopic examination affords no evidence of the resolution of the diatomic into monatomic molecules at the highest temperatures at which we worked.

Bands observed with 0.5 mgrm., using the Cadmium Arc.

1010° C.		855° C.	
3550	2990	3298	Series of bands from 2742 to 2724 and from 2724 to 2690 2650 <i>w</i> 2630 <i>w</i> 2510 2437 2435 2433 2410 2404 2399 2390
3416	2987	3216	
3392	2982	3170	
3374	2976	3070	
3358	2973	3063	
3343	2970	3027	
3325	2966	3000	
3314	2962	2990	
3298	2958	2967	
3284	2954	2962	
3246	2952	2954	
3233	2944	2924	
3215	2935	2864	
3203	2929	2860	
3195	2924	2848	
3185	2916	2846	2410
3176	2913	2843	2404
3170	2911	2835	2399
3164		2826	2390
3152		2824	
3142		2822	
3125		2806 <i>w</i>	
3116		2777	
3104		2750	
3097			
3074			
3070			
2064			
3055			
3047			
3044			
3035			
3027			
3023			
3015			
3010			
3005			
3000			
2995			

w = wide.

At 855° C. marked series of bands occur: four bands between λ 2742 and λ 2733, sharp narrow bands at λ 2717, λ 2710, λ 2696, λ 2693, and λ 2690. At 660° C. one faint band at λ 2806 was observed. No bands occur in any spectrum below 660° C. At 1175° C. the spectrum was extended at the red end for about 70 units farther than at 1010° C.

In measuring the wide bands recorded in the above lists the middle position of the bands has been taken. There is evidence that some of these bands could be resolved into series by using a different type of spectrograph.

DESCRIPTION OF PLATES.

PLATE 13.

Fig. 2.—Spectrum of 1 mgrm. of sulphur.

Fig. 3.—Spectrum of 8 mgrm. of sulphur.

PLATE 14.

Fig. 5.—Spectrum of sulphur vapour at constant pressure of 768 mm.

Tube 100 mm. long.

An Apparatus for the Direct Determination of Accelerations.

By the late Prince B. GALITZIN, For. Mem. R.S.*

The question of the determination of the acceleration of the true motion of the ground in various seismic phenomena, or of the motion in different parts of buildings, bridges, and all kinds of artificial structures, due to explosions, shocks, or oscillations of the ground, has a considerable theoretical and practical interest, since the investigation of these accelerations serves as a guide in the study of the mechanical forces by which these movements are caused. The knowledge of these forces is particularly important in the design of buildings of all kinds in seismological areas, and also for the calculation of various elements (ties or reinforcements) of structures which are often subjected to vibrations caused by the action of powerful engines by shifting of large masses (in the case of bridges or buildings on yielding foundations), by sudden shocks (in the case of ships armed with heavy guns), and so on.

The problem of the determination of the true magnitude of the accelera-

* The two papers, by Prince Galitzin, which follow, are translated from the originals, which appeared in the 'Bulletin of the Academy of Science of Petrograd' for 1915. Their publication in the 'Proceedings' has, for special reasons, been authorised by the Council of the Royal Society.

Prince Galitzin was elected a Foreign Member of the Royal Society on March 23, 1916, and died May 17 of the same year. The papers contain, therefore, the last work of a distinguished man of science. It was represented to the Council that they were of high scientific value, but inaccessible to most men of science, owing to their only having appeared in the Russian language.

Under these circumstances the Council felt justified in departing from the usual practice of not publishing communications that have already appeared elsewhere.—A.S.

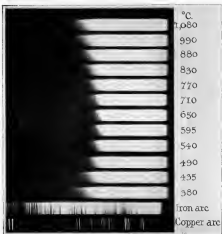


FIG. 2.

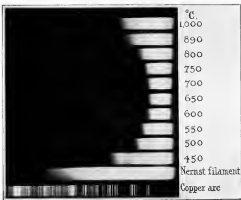


FIG. 3.

PLATE 13.

Fig. 2.—Spectrum of 1 mgm. of sulphur.

Fig. 3.—Spectrum of 8 mgm. of sulphur.

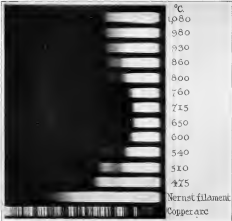


FIG. 5.

PLATE 14.

Fig. 5.—Spectrum of sulphur vapour at constant pressure of 768 mm.
Tube 100 mm. long.